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ORIGINAL ARTICLE

Self-assembly of poly(vinylidene fluoride)–polystyrene block copolymers in solution: Effects of the length of polystyrene block and solvent compositions

Yao Wu [a,b,1], **Lei Chen** [a,b,1], **Xiuyun Sun** [a,b], **Jie Xu** [c], **Guangxin Gu** [c,*], **Jieshu Qian** [a,b,*]

[a] *School of Environmental and Biological Engineering, Nanjing University of Science and Technology, Xiao Ling Wei 200, Nanjing 210094, PR China*
[b] *Jiangsu Key Laboratory of Chemical Pollution Control and Resources Reuse, Nanjing University of Science and Technology, Nanjing 210094, PR China*
[c] *Department of Materials Science, Fudan University, 220 Handan Road, Shanghai 200433, PR China*

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Abstract We report the first preliminary and extensive study on the solution self-assembly behaviors of poly(vinylidene fluoride)–*b*-polystyrene (PVDF–PS) block copolymers. The two PVDF–PS polymers we examined have the same length of PVDF block with number averaged repeating unit of 180, but distinctly different lengths of PS block with number averaged repeating unit of 125 and 1202. The self-assembly experiments were carried out in a series of mixture solutions containing a good solvent *N*,*N*-dimethylformamide and a selective solvent with different ratios. Our results showed that the self-assembly process was greatly affected by the two factors we examined, i.e. the length of the PS block and the solvent composition. We hope that our study could stimulate more research on the self-assembly of PVDF-containing polymers in solution.

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[*] Corresponding authors at: School of Environmental and Biological Engineering, Nanjing University of Science and Technology, Xiao Ling Wei 200, Nanjing 210094, PR China. Fax: +86 25 84315352 (J. Qian). Department of Materials Science, Fudan University, 220 Handan Road, Shanghai 200433, PR China. Fax: +86 21 65648837 (G. Gu).
E-mail addresses: guangxingu@fudan.edu.cn (G. Gu), qianjieshu@foxmail.com (J. Qian).

[1] These authors contribute equally to this work.

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1. Introduction

The self-assembly of block copolymers in selective solvents generates micelles with different structures, such as spheres [1], cylinders or wormlike micelles [2], and vesicles [3]. Factors affecting the morphologies of the micelles include the structure and length of each block, the choice of solvent or solvent mixture, the variation in temperature, *etc* [4]. Depending on the structure, one can classify the polymer block as coil, rod, or crystalline block [5]. Coil-like block is amorphous and forms swollen coils in a good solvent. The morphology of the micelles formed by the self-assembly of coil–coil block copolymers is determined by the contribution of three components, the free energy required to stretch the insoluble chain to fill the core, the interfacial free energy between the core block and the solvent, and the interactions between the corona chains [6]. One can change the morphologies of the micelles formed by coil–coil block copolymers from spheres to cylinders and vesicles by changing the block ratios[4a] and solvent compositions [4b]. Rod-like polymer has rigid and extended chains. Block copolymers with rod-coil structures are predicted to form disk-like micelles with a parallel alignment of the rigid blocks [7], or string-like micelles with the rod blocks packing as a helical twist along the string [8]. Crystalline block indicates that polymer chains are able to crystallize and form a folded lamellar structure [9]. The self-assembly process of the crystalline-coil block copolymers is usually dominated by the crystallization of the crystalline block, forming fiber-like micelles [10]. The crystallization-driven self-assembly process of a series of block copolymers containing a crystalline polyferrocenylsilane (PFS) block has been studied intensively by the collaboration of the Manners and the Winnik group [11], with recent extension to block copolymers containing a crystalline poly(3-hexylthiophene) (P3HT) block [12].

Poly(vinylidene fluoride) (PVDF) is an important fluorinated polymer with excellent properties and processability. Due to the presence of strong C–F bonds, the PVDF homopolymer possesses great chemical and thermal stability and thus has been widely used in many applications, such as building industry, petrochemical industry, chemical engineering, *etc*. Block copolymers containing a PVDF block can generate ordered structures and provide tailored properties based on the nature of the non-PVDF block. These PVDF block copolymers have found applications such as adhesives, surface modifiers, additives for resin gelification and hardening, and fuel cell membranes [13]. For examples, when used as proton exchange membrane, both PVDF–SPS (SPS = sulfonated polystyrene) diblock copolymer and SPS–PVDF–PS triblock copolymer have been reported to be able to phase separate in the bulk state to produce domains that facilitate the transportation of protons, showing higher proton conductivity than that of their random copolymer analogs or sulfonated polystyrene alone [14]. The Brinke and Loos group synthesized a series of PS–PVDF–PS and PtBMA–PVDF–PtBMA (PtBMA = poly(tert-butyl methacrylate)) block copolymers and used the lamellar structures formed by the solid state self-assembly of these PVDF block copolymers as templates to deposit nickel, a subsequent etching or hydrolysis of the non-PVDF block could generate PVDF/Ni nanocomposites [15]. Although the solution self-assembly of fluoropolymers has attracted many interests [16], the self-assembly of PVDF block copolymers in solution has not been described yet, probably because well-defined PVDF-containing block copolymers are difficult to synthesize and this is relatively rare [17].

In this paper, we report the first extensive study on the solution self-assembly of two PVDF–PS diblock copolymers, PVDF$_{180}$–PS$_{125}$ and PVDF$_{180}$–PS$_{1202}$ (the subscripts refer to the number average degree of polymerization), with the same PVDF block length but different PS block lengths. The structure of the PVDF–PS is presented in Scheme 1. The self-assembly experiments of the two polymers were carried out in a series of binary mixture solvents containing *N*,*N*-dimethylformamide (DMF) as a good solvent for both PVDF and PS blocks and a selective solvent, which is a good solvent for PS but non-solvent for PVDF. The experimental results showed that both the length of the PS block and the solvent composition have effects on the self-assembly behaviors of the PVDF–PS block copolymers. Our paper represents the first study of the self-assembly of PVDF-containing block copolymers in solution.

2. Experiment

2.1. Materials

Both PVDF$_{180}$-*b*-PS$_{125}$ (M_n = 11,500-*b*-13,000 g mol^{-1}, PDI = 1.2) and PVDF$_{180}$-*b*-PS$_{1202}$ (M_n = 11,500-*b*-12,5000 g mol^{-1}, PDI = 1.28) were purchased from Polymer Source Inc., Canada. *N*,*N*-Dimethylformamide (DMF, 99%) was purchased from Sigma–Aldrich, China. n-Butylacetate (BuAc, 99.7%) was purchased from Shanghai Aladdin Reagent Co., Ltd. Chloroform (99.0%), toluene (99.5%) and acetone (99.5%) were purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd. Cyclohexane (99.5%), 1,4-dioxane (99.5%), and anisole (98.0%) were purchased from Sinopharm Chemical Reagent Co., Ltd. All materials were used as received.

2.2. Micelle preparations

A typical micelle solution was prepared by adding 1.00 mg PVDF–PS polymer into 1.00 mL solvent mixture (c = 1.00 mg mL^{-1}) in a 5 mL vial, which was then heated at a certain temperature (60 °C for DMF/chloroform and DMF/acetone, 80 °C for DMF/cyclohexane, 100 °C for DMF/BuAc, DMF/toluene, DMF/anisole, and DMF/1,4-dioxane) for 1 h in an oil bath. The temperature of the oil bath was controlled by a IKATRON ETS-D5 (Germany) thermometer with a rated temperature fluctuation of 0.3 °C. Afterward, the heater was turned off and the solution was allowed to cool slowly to room temperature (ca. 20 °C) and age three days before TEM measurements.

For the kinetics study, 10.00 mg PVDF$_{180}$–PS$_{125}$ and 10.00 mg PVDF$_{180}$–PS$_{1202}$ were added into two 10 mL solvent mixtures (DMF/1,4-dioxane volume ratio = 80:20) in two 20 mL vials. The solutions were heated at 100 °C for 1 h, followed by slow cooling to room temperature (ca. 20 °C). DLS measurements were performed at different times after the sample preparation, 1 day, 4 days, 7 days, 10 days, 14 days and 18 days. At each time, 1 mL solution was placed into a new vial for DLS measurement. At the end of the experiment, both samples were also examined by TEM.